

INFLUENCE OF HYDROGEN SULPHIDE PRETREATMENT ON HYDROPYROLYSIS OF A BITUMINOUS COAL

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Abstract

The influence of 5% H_2S/H_2 pretreatment of a bituminous Beringen Belgian coal on HyPy is studied in a thermobalance. The presence of H_2S does not improve the total oil yield, but increases the oil evolution rate. Thus, HyPy can be performed at a temperature 60°C lower in H_2S/H_2 -HyPy than in normal HyPy, resulting in an increase in the efficiency of hydrogen utilization. Sulphur is added to coal during H_2S/H_2 pretreatment stage and is removed in the following HyPy stage, indicating that H_2S does not act as a real catalyst. A kinetic analysis shows that the activation energy in the initial stage of oil formation in H_2S/H_2 -HyPy is remarkably reduced as compared with that in H_2 -HyPy. It is suggested that H_2S acts as a hydrogen donor to improve hydrogen transfer and to generate the active sulphur radicals for easier saturation of free radicals formed pyrolytically.

Introduction

Hydrogen pretreatment of coal was reported to be effective in improving both the yield and the quality of the oil in the following hydropyrolysis (HyPy) (1). It is still interesting to find a way to accelerate the rate of oil formation at low temperature in order to increase the hydrogen utilization efficiency due to the decrease in the formation of light hydrocarbon gases.

It is known that H_2S can act as a hydrogen transfer catalyst and appears to be a hydrogen donor (2-5). The activation energy for hydrogen transfer and the temperature necessary to promote effective hydrogen transfer are bound to decrease (6,7). The reaction between H_2S and free radicals formed pyrolytically is much faster than that between H_2 and radicals, even with the addition of only a small amount of H_2S under lower temperature (8). According to several reports on coal liquefaction (9-11), 5% H_2S in H_2 seems to be enough effective to obtain the highest catalytic activity.

The purpose of this paper is to examine the influence of coal pretreatment with 5% H_2S in H_2 on HyPy using a thermogravimetry study. The comparison between the pretreatment under H_2 and H_2S/H_2 at 673 K and 3 MPa is investigated in detail while the effects of H_2S/H_2 pretreatment at other temperatures are simply compared. A kinetic analysis is attempted to obtain further information for the explanation of the H_2S function.

Experimental

A two-pin thermobalance with a sample of 0.1 g is used in this study. The apparatus has been described elsewhere (12). The on-line

gas analysis is carried out by gas chromatography with a methanizer using Ni as a catalyst for the quantitative detection of gas components CH_4 , C_2H_4 , C_2H_6 , CO and CO_2 .

Hydrogen pretreatment (H_2P) and $\text{H}_2\text{S}/\text{H}_2$ pretreatment ($\text{H}_2\text{S}/\text{H}_2\text{P}$) are performed under 3 MPa with a gas flow rate of 1 l/min and a heating rate of 5 K/min up to 673 K (or at other temperatures) for 30 min. In the H_2P -HyPy process, HyPy is run up to 1100 K directly after pretreatment, while in the $\text{H}_2\text{S}/\text{H}_2\text{P}$ -HyPy process, the reactor is first evacuated to remove H_2S for later analysis of the gas, HyPy is then operated under 3 MPa and a heating rate of 5 K/min with a gas flow rate of 1 l/min.

A bituminous Berigen Belgian coal is ground to less than 90 μm for this study. Its characteristics are given in Table 1.

The content of combustible sulphur in the pretreated coal and char is analysed by means of Carlo Erba Elemental Analyser (Model 1106) with a paropok column (1/4" X 0.8 m).

The data on gas composition obtained by G.C. is corrected in order to eliminate the influence of the time-lag in getting product gases to G.C.. The oil yield is given by carbon balance. The carbon content in char at various temperatures is analysed in our laboratory (13). The carbon content in oil is found to be $84 \pm 2\%$.

Kinetic analysis

The thermal decomposition of coal can be described as:

$$\frac{dx}{dt} = A \exp(-E/RT) (1-x)^n \quad (1)$$

Assuming first order for the rate of mass loss at a constant heating rate, we obtain:

$$\frac{dx}{dT} = \frac{A}{m} \exp(-E/RT) (1-x) \quad (2)$$

where m is the heating rate, x the decomposed fraction (on the decomposable basis, here based on the weight loss at 913 K at which oil evolution is ended) and A , E and R are the usual Arrhenius equation terms. The integration of equation (2), by using the integral approximation method (14), gives

$$\ln(-\ln(1-x)/T^2) = \ln\left(\frac{AR}{mE}\right) / (1+2RT/E) - E/RT \quad (3)$$

Since $2RT/E$ is much less than unity at moderate temperature and high activation energies, the value of $(1+2RT/E)$ is assumed constant. Thus, the kinetic parameters from equation (3) can be determined by plotting $\ln(-\ln(1-x)/T^2)$ versus $1/T$. For low activation energy, the value of $2RT/E$ can not be negligible. Equation (3) can be rewritten as:

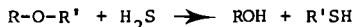
$$\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E) = \ln\frac{AR}{mE} - E/RT \quad (4)$$

A more accurate value of E is obtained by using the first approximate E and plotting $\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E)$ versus $1/T$.

Results and Discussion

1. Comparison of H_2P -HyPy and H_2S/H_2P -HyPy

The influence of pretreatment with 5% H_2S/H_2 on HyPy under 3 MPa and 5 K/min at 673 K for 30 min is first studied to compare the results obtained in H_2P -HyPy under same conditions. Figure 1 shows the comparison in yields of char, oil and gas. The conversion in H_2S/H_2P -HyPy is about 4% (wt%) higher than that in H_2P -HyPy. Before 880 K the higher conversion is mainly attributed to the higher oil yield while after 880 K it comes from the difference in gas yield. Figure 2 and 3 show the yields of CH_4 , C_2H_6 , CO and CO_2 . Before 1100 K the CH_4 yield is lower in H_2S/H_2P -HyPy than that in H_2P -HyPy, which may relate to the higher oil yield at lower temperature in H_2S/H_2P -HyPy because H_2S can change the route of cleavage of some bonds. Surprisingly, it is found that at higher temperatures, the difference in gas yield, which leads to higher conversion in H_2S/H_2P -HyPy, results from the increasing CO yield with an increase in temperature. In H_2P -HyPy, like HyPy, the evolution of CO is ended at about 1000 K. The reason why CO enhances with increasing temperature and more CO is formed might be that H_2S reacts with ether groups to form phenolic hydroxyl groups according to the following reaction (10):



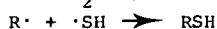
Then, hydroxyl groups decompose to CO at higher temperature (15,16).

Figure 4 shows the comparison of oil evolution rates in H_2P -HyPy and H_2S/H_2P -HyPy. It is clear that although the maximum oil yield is same in these two processes, the oil yield formed during the pretreatment stage is higher and the oil reaches the maximum yield more quickly in H_2S/H_2P -HyPy. This demonstrates that the reactions between H_2S and free radicals formed pyrolytically are much faster than that between H_2 and radicals. It is also observed that the oil evolution ends about 60°C earlier in H_2S/H_2P -HyPy as compared with H_2P -HyPy. Figure 5 gives the comparison of hydrogen utilization in H_2P -HyPy and H_2S/H_2P -HyPy. For the same oil yield, a high amount of total hydrogen in gaseous compounds means more hydrogen being consumed in the formation of hydrocarbon gases. One important factor in the economics of the coal hydrogenation process is the hydrogen consumption. For this reason, it is desirable that the formation of gaseous products which consume more H_2 be minimized while liquids are maximized. Thus, using H_2S pretreatment, HyPy can be performed at lower temperature, resulting in an increase in the efficiency of hydrogen utilization due to the decrease in the formation of light hydrocarbon gases. The study (17) on the reaction of H_2S with model compounds also found that the addition of H_2S reduced reductant consumption as much as three-fold whilst maintaining high oil yield levels when the reaction temperature was reduced by 60°C.

Table 2 gives the comparison of combustible sulphur content in H_2S/H_2 pretreated coal, H_2 pretreated coal and chars obtained in H_2S/H_2P -HyPy and HyPy. After H_2S/H_2 pretreatment the sulphur content in pretreated coal increases from 0.42% to 1.11% as compared with that in H_2 pretreated coal, showing that H_2S does not act as a real

catalyst. However, the sulphur content in char in H_2S/H_2 P-HyPy is almost the same as that in HyPy. This implies that the additional sulphur in H_2S/H_2 pretreatment stage will be removed in the following HyPy stage, leaving the sulphur content in char unchanged. Thus, it is suggested that H_2S acts as a hydrogen donor to improve the hydrogen transfer and the reactions between H_2S and coal follow free radical chain mechanism, involving the active sulphur radicals $\cdot SH$ as intermediate as follows:

in H_2S/H_2 pretreatment stage,



in the following HyPy stage,



Figure 6 gives the comparison of kinetic curves in H_2 P-HyPy and H_2S/H_2 P-HyPy. Table 3 lists the kinetic parameters. HyPy can be roughly divided into three stages: the pyrolytic stage at temperature below 750 K; hydrogenation in temperatures ranging from 750 to 850 K; and the hydrocracking stage at higher temperatures. In the pyrolytic stage the free radicals are mainly saturated by internal hydrogen while at the hydrogenation stage they are stabilized by gaseous hydrogen. The presence of H_2S decreases the apparent activation energy as much as four-fold in the pyrolytic stage as compared with that in the absence of H_2S , while it has no effect on the apparent activation energy in higher temperature stages. It is known that the bond energy of H_2 is greater than that of most C-H bonds whereas that for H_2S is not (18). According to data on the relative bond strengths most C-S bonds are cleaved much more rapidly than almost all C-C bonds (5). Thus, the saturation of free radicals by H_2S and the cleavage of the saturated radicals are much faster at the low temperature stage in H_2S/H_2 P-HyPy than that in H_2 P-HyPy.

It should be noted that HyPy in fixed-bed reactor, due to the slow rate of hydrogen diffusion and without solvent, seems to be more subject to mass transfer limitation (1). During H_2S/H_2 pretreatment stage, a considerable amount of oil is produced, which results in a decrease in agglomeration ability. Therefore, more H_2 will penetrate the coal to saturate the free radicals in the following HyPy stage, leading to an increase in oil evolution rate.

The H_2S/H_2 pretreatment of coal can be easier performed because H_2S is generated within the process. The problem is whether the sulphur content in oil will be increased, which leads to an additional cost in the treatment of oil. The studies (5,10) in coal liquefaction using H_2S/H_2 showed a very small increase in total sulphur in liquids and a very large increase in total sulphur in the residue. It might be possible to obtain the same quality of oil in H_2S/H_2 P-HyPy as in H_2 P-HyPy, but this needs to be proved.

2. Influence of different pretreatment temperature

Figure 7 shows the influence of H_2S/H_2 pretreatment temperature

ranging from 573 to 723 K under 3 MPa for 30 min on oil yield. The oil yield obtained in $H_2S/H_2P-HyPy$ indicates the same tendency as in $H_2P-HyPy$ (1). After 623 K, the oil yields in $H_2S/H_2P-HyPy$ and $H_2P-HyPy$ are higher than that in $HyPy$. The same oil yield produced in $H_2S/H_2P-HyPy$ and $H_2P-HyPy$ shows that the presence of H_2S does not improve oil yield. However, the oil yield obtained during H_2S/H_2 pretreatment stage is much higher than that obtained during H_2 pretreatment stage. In H_2P at 673 K, little oil is produced while in H_2S/H_2P at the same temperature about 25% of total oil in $H_2S/H_2P-HyPy$ is already formed. This further demonstrates that H_2S can reduce the activation energy for hydrogen transfer and the temperature necessary to promote effective hydrogen transfer.

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Table 1. Beringen Coal Analysis

Proximate Analysis(wt%, as received)		Ultimate Analysis(wt%,daf)	
Moisture	1.49	C	84.74
Ash	4.72	H	4.86
Volatile Matter	34.52	N	1.70
		O+S(by difference)	8.70

Table 2. Combustible sulphur Contents in Pretreated Coal and Char

Coal	Pretreated Coal 3 MPa,673 K,30 min		Char 3 MPa,1073 K		
	H ₂ P	H ₂ S/H ₂ P	HyPy	H ₂ S/H ₂ P-HyPy	
S(wt%,daf)	1.17	0.42	1.11	0.12	0.18

Table 3. Comparison of Kinetic Parameters in H₂S/H₂P-HyPy and H₂P-HyPy under 3 MPa and 5 K/min. Pretreatment: 3 MPa, 673 K

Process	Tem. Range (K)	Ea° (KJ/mol)	A (1/min)	Coef. Correlation
H ₂ P-HyPy	673-750	79.99	7.58x10 ⁶	0.979
	750-850	43.08	45.71	0.980
	850-913	74.31	5.10x10 ³	0.991
H ₂ S/H ₂ P-HyPy	673-750	20.17	0.71	0.977
	750-850	43.08	45.71	0.980
	850-913	74.31	5.10x10 ³	0.991

- Apparent activation energy obtained by $\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E)$ versus $1/T$.

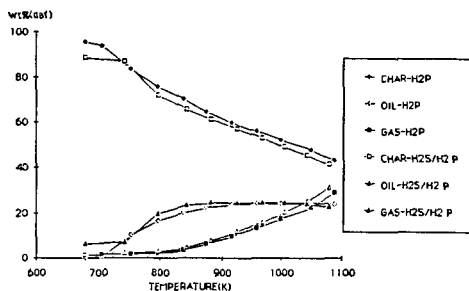


FIG 1 COMPARISON BETWEEN H₂P-HyPy AND 5% H₂S/H₂ P-HyPy IN YIELDS OF CHAR,OIL AND GAS. PRETREATMENT: 3 MPa, 673 K, 30 min

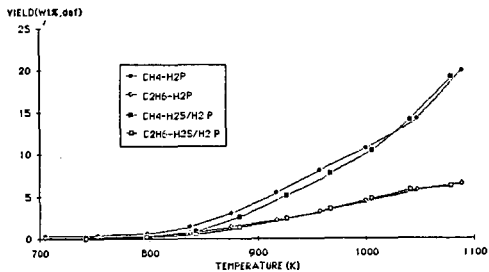


FIG 2 COMPARISON ON YIELDS OF CH₄ AND C₂H₆ BETWEEN H₂P AND 5% H₂S/H₂ P PRETREATMENT CONDITION: 3 MPa, 673 K, 30 min

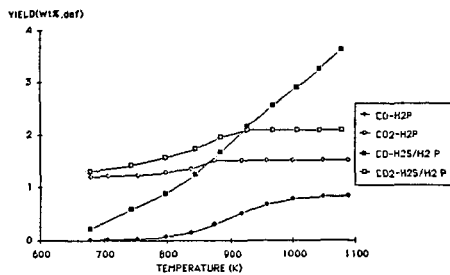


FIG 3 COMPARISON ON YIELDS OF CO AND CO₂ BETWEEN H₂P AND 5% H₂S/H₂ P PRETREATMENT CONDITION: 3 MPa, 673 K, 30 min

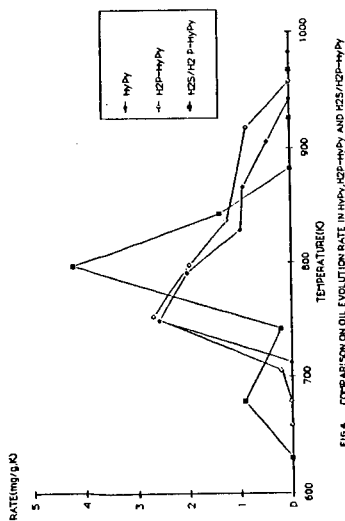


FIG 4 COMPARISON ON OIL EVOLUTION RATE IN H₂P-H₂P, H₂P-H₂P, AND H₂S/H₂P-H₂P AT 3 MPa, 5 K/min, 673 K, 30 min

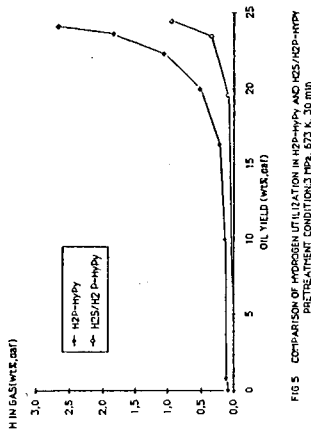


FIG 5 COMPARISON OF HYDROGEN UTILIZATION IN H₂P-H₂P AND H₂S/H₂P-H₂P PRETREATMENT CONDITIONS 3 MPa, 673 K, 30 min

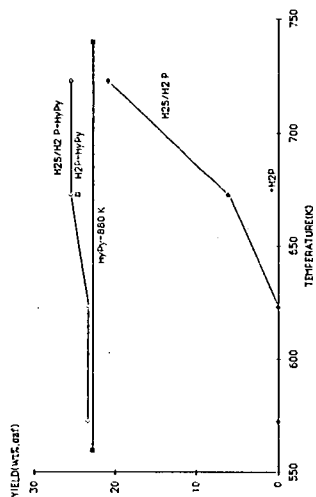


FIGURE 7 INFLUENCE OF PRETREATMENT TEMPERATURE ON OIL YIELD PRETREATMENT: 3 MPa, 5 K/min, 30 min

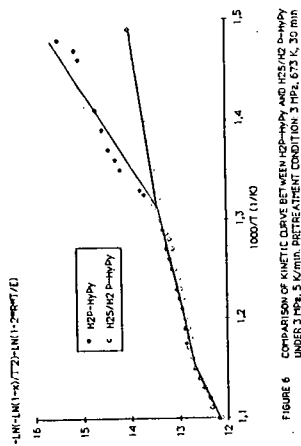


FIGURE 6 COMPARISON OF KINETIC CURVE BETWEEN H₂P-H₂P AND H₂S/H₂P-H₂P UNDER 3 MPa, 5 K/min, PRETREATMENT CONDITION 3 MPa, 673 K, 30 min